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Inge Tell

HYDROTHERMAL STUDIES ON FLUORINE AND BORON METAMORPHIC REACTIONS IN DOLOMITE

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NOMENCLATURE

T	Temperature.
^{o}K	degrees kelvin.
^{o}C	degrees centigrade.
P_{total}	isotropic pressure acting on the solid phases.
P_f	total pressure of the fluid phase.
P_i	partial pressure of gas species i.
f_i	fugacity of gas species i.
f_i^*	fugacity of the pure gas i.
X_i	mole fraction of species i.
K_p	thermodynamic equilibrium constant.
O.D.	outer diameter.
p.s.i.	pounds per square inch.
Dol	dolomite.
Cc	calcite.
Ch	chondrodite.
Tc	talc.
F	fluorite.
Di	diopside.
Tr	tremolite.
Q	quartz.
Bc	brucite.
S	serpentine.
Fb	fluoborite.
( )	small amounts of the phase.
↓	reversed reaction.

A great deal of experimental work concerning progressive metamorphic reactions in siliceous dolomites and limestones has been carried out since Bowen (1940) introduced his decarbonation series. There is also a good deal of information regarding the natural appearance of mineral assemblages in metamorphic calcareous rocks. These rocks show great mineralogical variation, and as far as contact metamorphism is concerned they have been the subject of extensive speculation regarding the effects of volatile compounds introduced by magmatic fluids.

The present study is based on hydrothermal investigations on the formation and stability of some fluorine- and boron-bearing minerals in carbonate systems. In experiments of this kind it is a matter of petrogenetic interest to establish equilibrium relationships between the mineral phases. In systems where volatile compounds play a significant role and where metasomatic processes may have occurred it is, however, not always realistic to premise equilibria conditions. Thus it must be stressed here, that this study does not aim at complete establishment of equilibrium relationships.

Although attention was mainly directed at the formation of the fluorine- and boron-bearing minerals, attempts were made to obtain information on paragenetically related silica-dolomite reactions. Accordingly, the possibility of catalytic effects of fluid phase fluorine on the stability of some silicates has been paid some attention.

The hydrothermal equipment used in this study was built by the author, and it should be remembered that the initial experimental series have been subjected to difficulties normally connected with the development period of a new laboratory.

The experiments were conducted in Nimonic 105, cold-seal, pressure vessels (Tuttle 1949). The pressure bombs were heated externally in vertical furnaces. Pressure was supplied by a pump using water as pressure medium. Pressures were measured on Aminco bourdon tube gauges with a maximum scale reading of 50000 p.s.i. Vessels were sealed off from the gauges after a run-up period, and the pressure was subsequently measured regularly. The accuracy of quoted pressures is believed to be within $\pm$50 bars.

Temperatures were controlled by regulators and measured by NiCr-Ni thermocouples. Thermocouples were placed in wells approximately 5 mm from the charges. The temperature difference between the thermocouple well and the position of the charge was measured by comparing readings obtained from a thermocouple placed in the well and a thermocouple placed in the main bore of the bomb. Temperature gradients between well and charge and along the length of the charge, (2 cm), depend on the applied furnace temperature. In this study the majority of runs have been conducted in the temperature range between 400 and 550^{o}C. The maximum temperature gradient measured within this temperature range was 7^{o}C. Calibration data recorded by this method show good agreement with data obtained from calibration of almost identical equipment with mantled

thermocouples (personal communication: Nitsch, K.H., Mineralogisch-Petrologisches Institut der Universität Göttingen, BRD). Temperature variation over the duration of the runs did not exceed $\pm 5^{\circ}C$. All runs have been corrected for the gradient differences and the temperatures given are believed to be within $\pm 10^{\circ}C$.

The charge was sealed in 3.3 mm O.D. x 2 cm long Au tubes. The fugacities of the gas species were not externally controlled by buffers. Accordingly hydrogen diffusion may occur from the pressure medium into the charge through the Au tubing. This may disturb the gas composition by causing reduction of CO_2 to graphite. The tubing was welded in a carbon arc. The tubes were weighed and placed in the pressure vessels. At the conclusion of a run, vessels were quenched in a stream of air for 10-20 minutes. The capsules were cleaned, and reweighed and runs which lost or gained more than 2 mg were considered unacceptable. Capsules were punctured and reweighed immediately. An audible gas efflux upon opening the capsules and constant weight were taken as indicating that the capsule had remained sealed during the run. The capsules were then dried to constant weight at $110^{\circ}C$ and reweighed. The amounts of CO_2 and H_2O in the gas phase were thus gravimetrically obtained. This method has been used by Metz (1966, 1967) and Johannes (1967).

The starting material consisted of natural dolomite, quartz, fluorite, talc, and tremolite. The boron component was added as B_2O_3. The dolomite from Långban contained 31.0% CaO, 20.2% MgO, and traces of Fe and Mn. Quartz, fluorite, and talc did not show any notable deviation from the theoretical compositions. Tremolite was not analysed.

It was carefully separated from a coarse grained calcite-tremolite aggregate. The X-ray diffraction pattern of the tremolite did not show any presence of other phases. Benzoic acid has been used in a few runs to provide an initial content of CO_2 in the gas phase. The starting material was finely ground and intensively mixed. The weight of the solid material in the charge was generally 100-120 mg. Maximum weight of added water was 25 mg. A small number of runs were performed with minor concentrations of HF in the added water.

IDENTIFICATION OF THE PHASES

The solid reaction products were identified by X-ray diffraction. For this purpose a Philips diffractometer unit (PW 1010+PW 1050/25) was used. Brass slides with a shallow (0.5 mm), rectangular cavity were used as holders for the samples. Scanning speeds were $\frac{1}{2}^{o}$ per minute. CuK_{α} radiation was used.

Sahama (1953) regards X-ray diffraction as the most reliable method to distinguish the humite minerals from each other. Previously reported d-values for the humite minerals, however, show obvious variation of the intensities of respective phases. Comparison of X-ray diffraction data for chondrodite compiled in table 1 reveals considerable discrepancies as regards intensities and distribution of reflexions presented by different investigators. A survey of reported d-values of the four humite mineral phases (e.g. Sahama op.cit., and van Valkenburg 1961) indicates that the X-ray method is not completely distinct as

identification basis. The different phases have many of their reflexions in common, and overlapping reflexions from other minerals in the system complicate the X-ray patterns. The reaction products are sometimes weakly crystallized, and even relatively small changes in pt-conditions between different runs seem to cause displacements, variation of intensities, and non-appearance of several reflexions. X-ray diffraction patterns for reactants and various reaction products are presented in figures 1, 2, and 7. Assuming actual formation of two or several of the humite minerals in this kind of system, the identification of a certain humite mineral would be difficult.

Although several initial mixtures have been used in attempts to obtain all humite phases as reaction products, no corresponding regularity in the variations of the d-values have been observed. The identification of products of incomplete reactions is characterized by pronounced uncertainty, and it has not been possible to establish preferential formation of any humite mineral at the beginning of the phase changes. As reactions proceed towards greater completion the reflexions show better uniformity regardless of starting material compositions. Although formation of minor amounts of other humite phases should not be excluded, observed d-values show best agreement with previously reported d-values for chondrodite.

On examination of figure 1 it is possible to observe displacements of some of the calcite reflexions. Values between 3.0369 Å and 3.0188 Å have been observed for the strongest reflexion of calcite. According to Harker and Tuttle (1955) the displacements are due to formation of Mg-calcite.

Chondrodite reflexions show similar displacements. One of its strongest reflexions shows displacement between 1.744 Å and 1.732 Å. No attempts have been made to explain these variations, but it is notable that the lower d-values represent weakly crystallized phases close to the synthesis boundary. Strongly displaced chondrodite reflexions have been observed in assemblages characterized by correspondingly extreme displacements of calcite reflexions.

FLUORINE REACTIONS

A. Occurrence of humite minerals

In some metamorphic silica-deficient dolomites and limestones minerals belonging to the humite group occur. The minerals of this group:

norbergite, $Mg(OH,F)_2 \cdot Mg_2SiO_4$
chondrodite, $Mg(OH,F)_2 \cdot 2Mg_2SiO_4$
humite, $Mg(OH,F)_2 \cdot 3Mg_2SiO_4$
clinohumite, $Mg(OH,F)_2 \cdot 4Mg_2SiO_4$

are generally considered as contact metamorphic minerals, and they typically appear in metasomatically zoned calcareous rocks adjacent to granite contacts (Turner 1968). Jones, Ribbe, and Gibbs (1969) give some examples of humite mineral occurrences connected with basic plutonic rocks. They have also been reported from regionally metamorphosed rocks lacking obvious connection to plutonic contacts (Wenck 1963, Trommsdorff 1966, Tröger 1967).

In petrogenetic interpretations of mineral assemblages in which humite minerals conspicuously occur, the fluorine

component is generally regarded as mobilized and metasomatically introduced. Metamorphic processes of this kind have been a field of considerable confusive discussion. They have invited petrologists to a variety of speculative theories regarding the properties of magmatic fluids. A great number of differently zoned aureoles have been described, but there is considerable disagreement between different authors concerning the interpretation of similar occurrences. There are contact metamorphic mineral assemblages where one author would be reluctant to refer to metasomatic processes, whereas, in a corresponding case, the separate fact that fluorite or humite minerals might occur, would be regarded as conclusive proof of metasomatism by another author.

Numerous occurrences of humite minerals have been described from the rocks of the Baltic shield, and in most of these cases the humite minerals are regarded as contact metamorphic. Among these occurrences there are, however, some which are not characterized by immediate vicinity to granite contacts (e.g. Magnusson 1925). These Precambrian rocks have achieved their present appearance by sequences of migmatization, repeated granite intrusions, and metasomatic processes, and such complicated conditions often make attempts futile to determine whether a certain fluorine-bearing assemblage has a regional metamorphic origin or may have formed in connection with granite intrusion. In terrains of regional metamorphism temperature gradients generally are indistinct, and "where bodies of granitic magma develop in, or are intruded into, deepseated rocks where temperatures are several hundred degrees, contact and regional effects may be indistinguishable" (Turner op.cit.). One early interpretation, which seems to be in

accordance with this way of looking at the matter, is that of von Eckermann (1922) who regards the chondrodite-bearing limestone of Pargas, Finland, described by Laitakari (1921), as a product of "regional pneumatolytic metamorphism".

Humite mineral structures and crystal chemistry have been studied by Larsen (1928), Taylor and West (1928, 1929), Rankama (1938), Sahama (op.cit.), Ribbe, Gibbs, and Jones (1968), and Jones, Ribbe, and Gibbs (op.cit.). Almost a century ago Sjögren studied their crystallography (1881 a,b, 1882 a,b,c, 1892, 1894). He also reviewed (1881 a) older literature on humite minerals and briefly described their geological appearance and paragenesis.

In contact metamorphic marbles chondrodite and clinohumite are the most common humite minerals. They generally appear with, and are intergrown with, forsterite (e.g. Tilley 1951 a, and Struwe 1958). Other minerals usually associated with the humite minerals are diopside, tremolite, phlogopite, chlorite, pennine, pargasite, and spinell, and, in some cases, fluorite and talc. Serpentinization of humite minerals is commonly observed.

Mineral associations, where one or several of the minerals mentioned above sometimes are lacking, have been reported by Eskola (1914), Emerson (1917), Laitakari (op.cit), von Eckermann (1922, 1923), Barth (1924), Magnusson (1925, 1929, 1930 a,b, 1940), Geijer (1936), Rankama (op.cit.), Sadashivaiah and Ghosh (1953), Muthuswami (1958), Bradshaw and Leake (1964), Kowalski (1966), Trommsdorff (1966 a), and Shimazaki (1968 a,b). One of the most detailed descriptions is that of the Kaveltorp area in the Ljusnarsberg ore district, Central Sweden, by Magnusson (1940), who observed the following sequence of

assemblages:

dolomite

ophicalcite consisting of forsterite or clinohumite

diopside accompanied by clinohumite or chondrodite

actinolite with chondrodite

tremolite with chondrodite, fluorite, and talc

antophyllite-cummingtonite with fluorite and talc.

The humite minerals are abundant in the diopside and actinolite zones and gradually disappear in the tremolite zone. Similar occurrences presented in descriptions of comparative completeness are those of Suian, Korea (Watanabe 1943), Broadford, Skye (Tilley op.cit.), and Someo and Frasco in the Lepontine Alps, Switzerland (Trommsdorff 1966 b).

Some occurrences differ in appearance from those reviewed above. Geijer (1928) has reported an association consisting almost exclusively of chondrodite and magnetite. Geijer also emphasizes, (1958), that among sulphides associated with humite minerals the dominance of galena and sphalerite is notable. According to him copper and iron sulphides rarely occur with humite minerals.

Chondrodite and clinohumite thus have been reported from a considerable number of localities, and it would be an exaggeration to regard them as rare minerals. Humite is probably not quite so common, but it is occasionally associated with the two more common minerals of the group. The fourth mineral, norbergite, has only been reported from a few places. Geijer (1926) described an assemblage of norbergite, tremolite, and Mg-ortite, and Larsen, Bauer, and Berman (1928) have observed it in coarse crystalline limestone,

where it occurs with and partly surrounds chondrodite.

B. Probable experimental reactions

Previous synthetical production of humite minerals has been reported by Rankama (1947), van Valkenburg (op.cit.), and Christie (1965). These investigations, however, were carried out on a purely synthetical basis, and no attention was paid to equilibria conditions or influence of volatile components.

In the present study natural dolomite, quartz, and fluorite have been used as starting materials. Dolomites and limestone containing quartz and other silicate minerals are common in nature. According to Koritnig (1951), Friedman and Sanders (1967), and Carpenter (1969) it is geochemically valid to assume primary occurrence of fluorine in sedimentary calcareous rocks. Such primary fluorine may probably be concentrated by mobilization and subsequently involved in metamorphic reactions. Irrespective of whether this has been the case, or fluorine has been introduced by magmatic fluids, in an experimental work of this kind, it is most convenient to add the fluorine component as the mineral fluorite.

An examination of a system, where dolomite, quartz, and fluorite are employed as original phases, makes it probable to assume the following reactions as relevant:

$$3\ \text{dolomite} + 1\ \text{quartz} + 1\ \text{fluorite} \rightleftharpoons 1\ \text{norbergite} + 4\ \text{calcite} + 2\ CO_2 \qquad (1)$$

$$5\ \text{dolomite} + 2\ \text{quartz} + 1\ \text{fluorite} \rightleftharpoons 1\ \text{chondrodite} + 6\ \text{calcite} + 4\ CO_2 \qquad (2)$$

$$7\ \text{dolomite} + 3\ \text{quartz} + 1\ \text{fluorite} \rightleftharpoons 1\ \text{humite} + 8\ \text{calcite} + 6\ CO_2 \qquad (3)$$

9 dolomite + 4 quartz + 1 fluorite $\rightleftharpoons$ 1 clinohumite +

+ 10 calcite + 8 CO_2 (4)

Theoretically the reactions above would produce anhydrous phases. The humite minerals, however, always contain OH-groups. Because water generally not is completely absent in contact metamorphic processes connected with metasomatism, it does not seem consistent with natural conditions to regard reactions (1)-(4) as a realistic basis for experiments.

What kind of reactions may then be expected to produce humite minerals? Is there any physico-chemical connection between the appearance of commonly coexisting phases, notably forsterite, diopside, and tremolite, and the formation of humite minerals? The most conspicuous chemical difference is that fluorine enters a silicate-carbonate system, but this does not necessarily mean that the fluorine-bearing phases form in the same metamorphic stages and under similar physical conditions as the accompanying silicates.

It is generally accepted as a fact that tremolite and talc appear as early products of metamorphic reactions in siliceous dolomites. There has been less agreement on the question whether tremolite or talc is the first phase to form by these reactions. Bowen (op.cit.) and Tilley (1951 b) expressed different opinions on the question. Metz and Winkler (1963), Metz, Puhan, and Winkler (1968), and Metz and Puhan (1970) have shown that talc should be the first mineral to form. According to Skippen (1967) formation of talc is not possible if the mole fraction of CO_2 in the gas phase is greater than approximately 0.5. With rising temperature decarbonation and dehydration reactions cause various

paragenetic assemblages. Experimental and calculated equilibria data for such reactions in the system $CaO-MgO-SiO_2-CO_2-H_2O$ have been presented by Skippen (op.cit.) and Metz and Trommsdorff (1968). If fluorine is primarily present in this system under conditions of progressive metamorphism it will sooner or later participate in the reactions. Tentative experiments with mixtures of dolomite, quartz, and fluorite, according to reactions (1)-(4) but in the presence of water, have shown that fluorite is not affected when the first reaction of dolomite and quartz to talc occurs. This implies that the fluorine component probably reacts with a preexisting metamorphic silicate. Possible reactions are:

$$1\ \text{talc} + 9\ \text{dolomite} + 4\ \text{fluorite} \rightleftarrows 4\ \text{norbergite} + 13\ \text{calcite} + 5\ CO_2 + 1\ H_2O \qquad (5)$$

$$1\ \text{talc} + 7\ \text{dolomite} + 2\ \text{fluorite} \rightleftarrows 2\ \text{chondrodite} + 9\ \text{calcite} + 5\ CO_2 + 1\ H_2O \qquad (6)$$

$$3\ \text{talc} + 19\ \text{dolomite} + 4\ \text{fluorite} \rightleftarrows 4\ \text{humite} + 23\ \text{calcite} + 15\ CO_2 + 3\ H_2O \qquad (7)$$

$$1\ \text{talc} + 6\ \text{dolomite} + 1\ \text{fluorite} \rightleftarrows 1\ \text{clinohumite} + 7\ \text{calcite} + 5\ CO_2 + 1\ H_2O \qquad (8)$$

Elimination of talc by simple dehydration reactions like:

$$1\ \text{talc} + 1\ CO_2 + 1\ \text{fluorite} \rightleftarrows 1\ \text{norbergite} + 3\ \text{quartz} + 1\ H_2O$$

is probably incongruous because humite minerals never occur associated with quartz. Assuming elimination of quartz in this type of system by subsequent crystalline reaction or by metasomatic solution, and introduction of fluorine by similar processes, however, would allow speculation on almost

any reaction. Considering the condition that talc only rarely occurs with humite minerals, reactions (5)-(8) must be regarded as dubious. Judging from natural mineral assemblages it would be likely to assume fluorine reactions with tremolite, diopside, and forsterite, but because it is desirable to investigate any effect of fluorine on silica-deficient dolomite subjected to progressive metamorphism, reactions (5)-(8) have been chosen as basis for a preliminary series of experiments. These reactions directly correspond to reactions (1)-(4) with initial addition of water. The starting materials dolomite, quartz, and fluorite have been mixed with water in amounts chosen to provide a wide range of variation of the composition of the gas phase. Talc has been initially added in a number of runs, and proportions of reactants have been varied according to the theoretical reactions in attempts to obtain the complete humite mineral series.

C. Experimental results

In order to establish minimum values of humite mineral formation a number of experiments have been performed with unsealed tubes at P_f=10500, 15000, 22500, and 30000 p.s.i. The results of experiments are given in table 2, 3, and 4 and shown graphically in figure 3.

Natural metamorphic conditions are almost never characterized by $P_f=P_{H_2O}$. Contact metamorphic processes, however, may provide low partial pressures of CO_2, and since the humite minerals commonly appear in contact metamorphic environments, the possibility of low values of P_{CO_2} should not be ignored. According to the phase rule reactions (5)-(8) are divariant reactions for the case in

which $P_{CO_2}+P_{H_2O}=P_f=P_{total}$. The gas composition-temperature dependence of humite mineral formation has been studied at 2000 bars. The run conditions and results of experiments arranged according to reactions (1), (2), and (6) are listed in tables 5, 6, 7, and 8 and shown graphically in figure 4. Runs with no or only very small amounts of initially added water conducted in the vicinity of the synthesis boundary result in incomplete reactions. CO_2 dominates in the gas phase, and the small amounts of water (between 0.5 and 2 mg) lead to considerable inaccuracy.

If CO_2 is allowed to disappear, fluorite reacts with the silicate and carbonate phases between 300 and 380°C for pressures between 700 and 2000 bars respectively. If CO_2 is previously formed by reaction between dolomite and quartz and contributes to the composition of the gas phase the participation of fluorite in reactions occurs at higher temperature.

The results of the experiments indicate that the fluorine component does not participate in the initial phase changes in the system. Reactions between quartz and dolomite occur at obviously lower temperatures than fluorine reactions. Talc is the most prominent phase resulting from initial reactions.

According to Tröger (op.cit.) only minor substitution of F for OH is possible in natural talc. This seems to be valid for synthetic talc as well. There is no evidence for initial participation of fluorine in the hydrothermal reactions by substitution for OH-groups in talc.

The stability boundary for the phases chosen as starting materials lies slightly above 500°C at P_f=2000 bars.

For mole fractions of CO_2 between 0.0 and 0.4 the boundary rises from 380 to 500°C. Above this boundary formation of chondrodite occurs. Stability relations of talc and tremolite presented by Skippen (op.cit.) indicate that talc is not stable in this pt-field. Assuming stability relations of talc according to Metz and Puhan (op.cit.), chondrodite formation occurs in the stability field of talc. Results obtained in this investigation indicate reaction between fluorite, talc, and dolomite. Metastable formation of talc, however, is very common in hydrothermal experiments concerning Mg-bearing silicate systems. The lack of general agreement as regards stability relations of talc and tremolite makes it difficult to make conclusions regarding fluorine-silicate reactions in which the erroneous influence of metastable phases is eliminated. Assuming metastable survival of talc, its subsequent reactions with fluorite and dolomite may represent either a metastable equilibrium or a synthesis boundary. Results given in table 8 represent reversed reactions. In a first stage these runs were conducted sufficiently above the previously established stability boundary of chondrodite. Maintaining P_f at 2000 bars the temperature was then reduced to values below the stability boundary. Reversal of reactions proceeds very slowly, but parallel runs give conclusive proof that there is a stability boundary below which chondrodite reacts back to talc.

Quantitatively chondrodite formation depends on the composition of the gas phase. The reaction being mainly a decarbonation and fluorination reaction, a high initial proportion of CO_2 causes attainment of equilibrium composition of the gas phase already by comparatively weak fluorine reaction. It is possible that high values of P_{CO_2} in

combination with low reaction rates causes uncertainty as regards establishment of equilibrium. Parallel runs with varying duration but identical initial composition were conducted immediately adjacent to the chondrodite stability boundary. For runs with durations less than 2 weeks the reaction rate may be a significant factor resulting in estimation of to high formation temperatures for chondrodite. Runs with durations between 5 and 10 weeks do not show any difference as regards crystalline products.

The reactions involve decarbonation from the first stage of the reaction. For gas phases containing more H_2O than CO_2 this condition could be a source of inaccuracy in runs adjacent to the chondrodite stability boundary. This is shown schematically in figure 5. Assuming mineralogical and pt-changes along the curve B-D in figure 5, where A represents the formation boundary of chondrodite, CO_2 and chondrodite will be subsequently observed at D. If, in contrast, the value of P_{CO_2} could have been experimentally adjusted during the runs, reactions would occur along C-D. It is possible that phases observed at D, resulting from a reaction P→D, would not include chondrodite, because the amount of chondrodite produced according to this kind of reaction would be insufficient for X-ray detection.

The possibility of different results of similar reactions are, however, hardly contradictory. The two types of experimental conditions outlined above merely represent two sets of probable natural conditions. In a siliceous dolomite subjected to progressive metamorphism, equilibrium may be maintained in the gas phase and between the solid phases over wide temperature intervals without essential mineralogical

reactions. It is likely that the humite minerals in such cases only to a relatively limited extent contribute to the composition of the gas phase by their formation. There are, on the other hand, petrological systems characterized by restricted mobility of CO_2 and H_2O during metamorphism (Melson 1964). Such conditions allow high values of P_{CO_2} to build up successively in limited volumes of rock. In decarbonation reactions of this type humite mineral formation may influence the equilibrium composition of the gas phase. The experimental conditions of this investigation correspond to a situation of natural metamorphism characterized by continuously rising P_{CO_2}.

Fluorine and silica both react with dolomite in certain stages of metamorphism. It is obvious that the presence of fluorine in the system $CaO-MgO-SiO-CO_2-H_2O$ reduces the hydrothermal stability of talc by formation of chondrodite. The behaviour of fluorine and silica may therefore, to a certain extent, be regarded as a kind of competition. It is important to find out whether the relative quantity of silica has any influence on humite mineral stability in a system subjected to pt-changes. It is also a matter of interest to establish whether fluorine affects other mineral equilibria in the system.

Initial mixtures characterized by less silica deficiency than those arranged according to previously outlined reactions have been employed in a number of runs. The run conditions and results of experiments with higher initial silica proportion are given in table 9 and shown graphically in figure 6. Reactions in a system consisting of dolomite, quartz, and fluorite in the proportions 10/10/1, plus initially

added water, primarily result in production of talc. Fluorine reactions are obviously much more incomplete in systems richer in silica. The first occurrence of chondrodite was observed at approximately 40°C higher temperatures than for more silica deficient systems. Talc, dolomite, fluorite, and chondrodite coexist over an extensive pt-field (cf. figure 6). These observations are probably not mainly due to insufficient duration of the runs or identification difficulties caused by the lower proportion of chondrodite formed in the system (cf. figure 1 and 2). It is likely that the humite minerals fail to crystallize if the fluid phase is too rich in silica, and if the silica is not employed for stable formation of tremolite, diopside, or forsterite.

It has been shown previously that talc, dolomite, and fluorite react to chondrodite at lower temperatures. The field of coexistence of these minerals under the prevailing conditions is possibly caused by silica saturation of the gas phase. As fluorination reactions employ Mg for chondrodite formation, excess silica produced by breakdown of talc gives a silica saturated gas phase which may disturb humite mineral formation. At higher temperatures the excess silica is engaged in formation of tremolite and diopside. This seems to favour the formation of chondrodite. The composition of the gas phase thus probably varies not only with respect to the proportion of CO_2 and H_2O. Metasomatic mobilization of Si and F may influence equilibria reactions, but the present knowledge of solubility conditions of fluorite and quartz does not cover silicate-carbonate systems. Stübel (1965) has shown that the solubility of fluorite in water rises with rising pressure. Kennedy (1944, 1950) has investigated the

solubility of quartz in water. Ellis and Mahon (1964) presented solubility data on quartz and fluorite in water. Barnes (1967, pp. 388-393) has given a review of other investigations of quartz and fluorite solubility. The information given by these investigators is not sufficient to allow any conclusions regarding the precise effects of dissolved components on the solid phases of this system. The quantity of silica dissolved in the gas phase during the reaction, however, possibly is higher than the quantity of fluorite. Assuming a negative effect of excess silica on humite mineral formation would be in agreement with the fact that humite minerals generally occur with forsterite and in other silica-deficient associations.

To check the behaviour of fluorine in relation to tremolite at lower temperatures a number of runs with tremolite, dolomite, and fluorite have been made. The run conditions and results of experiments are given in table 10. In figure 7 X-ray data of the reaction products of run number 138 are compared to those of run number 170. Although the values of P_{CO_2} of the gas phases are approximately the same, and the temperature of the run with initially added tremolite is lower, there is a distinctly stronger formation of chondrodite in the run with tremolite. The amount of chondrodite formed in run number 170 may be compared to that of run number 106 (cf. figure 1).

The Mg/Si ratio is approximately the same in runs according to reaction (6) as in the runs with initially added tremolite presented in table 10. Tentative runs, in which various proportions of the starting materials tremolite, dolomite, and fluorite were employed, indicated that the

fluorine component first affects coexisting tremolite and dolomite at pt-conditions similar to those characterized by chondrodite formation according to reaction (6).

According to Metz (1967), and Skippen (op.cit.) forsterite may form by reaction between tremolite and dolomite. Assuming that fluorine reaction favours the formation of forsterite, the following reaction could be significant:

$$1 \text{ tremolite} + 13 \text{ dolomite} + 2 \text{ fluorite} \rightleftharpoons 4 \text{ forsterite} + 2 \text{ chondrodite} + 17 \text{ calcite} + 9\ CO_2 + 1\ H_2O \quad (9)$$

Fluorine may, however, employ the Mg and Si components quantitatively, if clinohumite is formed:

$$1 \text{ tremolite} + 13 \text{ dolomite} + 2 \text{ fluorite} \rightleftharpoons 2 \text{ clinohumite} + 17 \text{ calcite} + 9\ CO_2 + 1\ H_2O \quad (10)$$

If simultaneous formation of different skarn silicates as well as more than one member of the humite group is to be allowed for, it would be possible to speculate on a great number of reactions.

The appearance of one or several skarn silicates may be qualitatively established, but considering the identification problems as regards the experimentally produced humite phases, a precise study of fluorine reactions involving catalytic effects would be difficult. The eventuality of forsterite formation influenced by fluorine reactions is satisfied by the experiments with starting material proportions according to reaction (9) and (10). The results, however, do not show any production of forsterite.

Tentative reactions at temperatures around 650°C have shown that chondrodite appears in association with forsterite

at higher temperatures. Runs with excess fluorite up to 750°C yielded chondrodite and calcite in connection with high values of P_{CO_2}. One experiment conducted in open capsule at 730°C with this mixture resulted in formation of monticellite, chondrodite, calcite and an unidentified phase.

As regards the possibility of catalytic effects of fluorine in the gas phase, there is nothing that indicates that the presence of fluorine in the system would facilitate formation of tremolite or other skarn silicates. This investigation, however, neither provides enough data nor sufficient accuracy to allow comparison with previously published experimental data on tremolite and diopside formation in systems without fluorine.

D. Thermodynamics

The information obtained from the experimental data is far from adequate as a basis of a theoretical analysis of the phase relations among the minerals under consideration. A thermodynamic treatment of the reactions would require precise knowledge of the phases involved in the reactions. Theoretically several reactions may lead to formation of humite minerals. Fluorine affects the stabilities of talc and tremolite associated with dolomite. Reactions with diopside and forsterite would probably also yield humite minerals. Considering the identification problems there is no guarantee that chondrodite is the only humite mineral produced.

According to Munoz and Eugster (1969) the influence of the HF fugacity is of minor importance in a carbonate system. The bulk chemistry of the C-O-H-F system is very similar to that of the C-O-H system. The present system,

however, includes silicate reactions, and silica dissolved in the gas phases has been assumed as significant for the appearance of humite minerals. It is likely that it is an oversimplification to regard H_2O and CO_2 as the only significant species in the gas phase. Even if H_2O and CO_2 are regarded as the main species in the gas phase, small amounts of dissolved silica and fluorite could be important to humite mineral equilibria. Available data (cf. Barnes 1967 pp. 388-393) do not allow conclusions concerning the activities of all species which may influence the humite mineral equilibria. The activities of coexisting calcite, dolomite, and humite minerals were not taken into account. They probably do not equal 1.

Although objections can be made against the significance of a theoretical treatment of the phase relations, experimental data according to reaction (6) provide a basis for some approximate calculations. This reaction can be written:

$$Mg_3Si_4O_{10}(OH)_2 + 7\ CaMg(CO_3)_2 + 2\ CaF_2 \rightleftharpoons 2MgF_2 \cdot 2Mg_2SiO_4 + 9\ CaCO_3 + 5\ CO_2 + 1\ H_2O$$

If all solids are assumed to be present in their standard states, the equilibrium constant is given by the fugacity product:

$$K_P = f_{CO_2}^5 \cdot f_{H_2O} \qquad (11)$$

In order to relate fugacities and mole-fractions, it is necessary to assume ideal mixing of CO_2 and H_2O. According to Franck and Tödheide (1959) a gas phase consisting of CO_2 and H_2O represents ideal mixture over the range of

pt-conditions applied to the system in this investigation. According to Lewis and Randall (see Denbigh 1957) the fugacity, f_g, of a gas in a gas mixture may be written:

$$f_g = f_g^* \cdot X_g \qquad (12)$$

The quantity f_g^* represents the fugacity of the pure gas at the temperature and total gas pressure being considered. X_g is the mole-fraction of the gas in the gas mixture.

The fugacities of CO_2 and H_2O may be calculated by relating experimental gas composition data and fugacities of pure gases:

$$f_{CO_2} = f^*_{CO_2} \cdot X_{CO_2} \qquad (13)$$

$$f_{H_2O} = f^*_{H_2O} \cdot X_{H_2O} \qquad (14)$$

Fugacity coefficents for H_2O at 2000 bars for the temperature interval between 200 and 1000°C have been published by Holser (1954). Fugacity coefficients for CO_2 at 1400 bars and less were given by Majumdar and Roy (1956) and above 1400 bars by Skippen (op.cit.). The fugacity data for CO_2 used in this investigation have been calculated by Metz (personal communication).

Equations (13) and (14) may be substituted into equation (11) to give the following relationship:

$$\log K_P = 5 \log (f^*_{CO_2} \cdot X_{CO_2}) + \log (f^*_{H_2O} \cdot X_{H_2O}) \qquad (15)$$

The equilibrium constant may be calculated for specified temperatures by deriving the gas composition data from the experimentally determined equilibrium curve in figure 4 and

solving equation (15) for the fugacities of species. Data for this calculation are listed in table 11. By plotting the equilibrium data obtained from equation (15) against the reciprocal temperature according to the following equation:

$$\frac{d \ln K_P}{d 1/T} = - \frac{(\Delta H)_P}{R} \qquad (16)$$

the heat of reaction $(\Delta H)_P$ is obtained in the form of a graph presented in figure 8. The deviation from a straight line is negligeable, and the variation of the heat of reaction with temperature accordingly is small. Despite the sources of uncertainty discussed previously the consistency of the calculated data indicate that the experimental chondrodite formation may represent an equilibrium reaction according to reaction (6).

BORON REACTIONS

Boron is an element that is believed to enter readily into volatile compounds. Magnesian borates forming parageneses with magnesian silicates and carbonates in contact aureoles indicate that boron may be introduced by aqueous gases. The appearance of some boron bearing minerals indicate that their formation is not restricted to narrow and well defined pt-conditions. According to Tröger (op.cit.) the boron minerals ascharite, ulexite, and danburite appear both in sedimentary-diagenetic and in low grade metamorphic parageneses. Magnesian borates occurring in mineral assemblages characterized by contact metamorphism are

ludwigite, fluoborite, and kotoite.

Participation of boron in endogenetic reactions is probably not as common as corresponding fluorine reactions. It appears, however, that there exists a relationship between boron and fluorine mineralization. Tilley (1951 a) has made a study of the boron-fluorine metasomatism in the dolomites of the Broadford area of Skye, Scotland. In the silica-deficient parts of this aureole fluoborite is intimately associated with chondrodite. In the Suian aureole, Korea, described by Watanabe (op.cit.), boron-fluorine metasomatism has caused formation of clinohumite, chondrodite, kotoite, and ludwigite. Watanabe also gives a review of a number of other boron-fluorine parageneses. Chesterman and Bowen, Jr. (1958) reported an occurrence of fluoborite associated with humite minerals in a dolomite in San Bernardino County, California.

According to Shabynin (1959) borates are usually concentrated in the outer zones of metasomatic columns consisting of forsterite (clinohumite) or phlogopite skarns. Although borate mineralization in many cases is clearly connected with postmagmatic metasomatism, it also may occur in connection with magmatic, i.e. progressive, metamorphism.

In order to obtain information on the behaviour of boron and fluorine in hydrothermal systems an experimental series aiming at the formation of the magnesium fluoborate fluoborite has been performed. Hydrothermal formation of fluoborite, $Mg_3[F_2(OH)|BO_3]$, has been accomplished according to the following reaction:

$$6 \text{ dolomite} + 2 \text{ fluorite} + 1\ B_2O_3 + 1\ H_2O \rightleftarrows 2 \text{ fluoborite} + 8 \text{ calcite} + 4\ CO_2 \qquad (17)$$

It is likely that solution equilibria form the basis for the crystallization of fluoborite. Accordingly reaction (17) can not reflect a mineralogical equilibrium between the phases. Borate mineralization of dolomite, however, probably involves a certain degree of decarbonation, which makes the P_{CO_2}-value a significant factor. The gas composition-temperature dependence of fluoborite formation has been studied at 2000 bars. The run conditions and results of experiments arranged according to reaction (17) are listed in table 12 and shown graphically in figure 9. X-ray diffraction patterns of starting materials and reaction products are given in figure 10. At very low X_{CO_2}-values (<0.1) fluoborite appears at temperatures below 400°C. At X_{CO_2}-values between 0.2 and 0.7 the reactions start at approximately 430°C. The reactions, however, are characterized by a general lack of completeness. Over a temperature interval of more than 100°C (striated area of figure 9) reaction products coexist with starting materials. In spite of long duration of the runs (>60 days) it has not been possible to obtain a more complete conversion of the starting materials to fluoborite and calcite in this area.

It is difficult to establish a synthesis boundary for fluoborite because its first appearance is characterized by very weak X-ray reflexions. The governing factor regarding the gas composition is decarbonation according to reaction (17). This means that fluoborite formation starts at $P_{CO_2}=0$. It is possible that it may appear already during the run-up period. Accordingly at least part of the fluoborite observed in the field in which starting materials coexist with reaction products may be the result of reaction at low

values of P_{CO_2}. In combination with the weak X-ray reflexions this fact makes a quantitative estimation of fluoborite stability uncertain. In runs where benzoic acid has been initially added the first appearance of fluoborite lies at approximately 450°C. This indicates that although fluoborite may appear at low temperatures of metamorphism, already low to moderate amounts of CO_2 in the gas phase disturb or retard reactions. It is likely that the limits of error regarding fluoborite formation considerably exceed the corresponding limits of fluorine reactions in this investigation.

SUMMARY AND CONCLUSIONS

The study reported in this thesis is an investigation of metamorphic fluorine and boron reactions in dolomite. The reactions considered include humite mineral formation in siliceous dolomite and fluoborite formation in non-siliceous dolomite. Fluorination data have been obtained for the reaction:

$$1 \text{ talc} + 7 \text{ dolomite} + 2 \text{ fluorite} \rightleftharpoons 2 \text{ chondrodite} + 9 \text{ calcite} + 5\ CO_2 + 1\ H_2O$$

Chondrodite formation was also established by reaction between tremolite, dolomite, and fluorite.

Preliminary experimental measurements were made for the reaction:

$$6 \text{ dolomite} + 2 \text{ fluorite} + 1\ B_2O_3 + 1\ H_2O \rightleftharpoons 2 \text{ fluoborite} + 8 \text{ calcite} + 4\ CO_2$$

Chondrodite formation has been studied at the total pressure of 2000 bars as a function of temperature and gas composition. The results are given as isobaric plots of the mole-fraction of CO_2 against temperature. In a silica-deficient system chondrodite appears between approximately 430 and 490°C, if the gas phase contains more H_2O than CO_2. If the gas phase contains more CO_2 than H_2O chondrodite formation occurs at temperatures slightly above 500°C. For the case in which $P_{total}=P_{H_2O}$, chondrodite appears at 300, 350, and 375°C for total pressures of 700, 1000, and 2000 bars respectively. The results indicate that fluorination reactions depend on the composition of the gas phase and the silica content of the solid phase system. Chondrodite is the only humite mineral produced by fluorination reactions of the present work. The assemblage chondrodite and calcite is stable to temperatures of at least 720°C.

Thermodynamic treatment of the results indicate that the chondrodite formation represents a divariant equilibrium. In this case, however, a petrogenetic conclusion based solely on equilibrium data calculated from the experimental results of this investigation would be of dubious value. The results are compatible with equilibrium, but there are several reasons to believe that it is not adequate to summarize humite mineral formation in one reaction. One of these reasons is the fact that humite mineral parageneses generally are characterized by forsterite, tremolite, and diopside. Talc is only rarely associated with humite minerals. In addition agreement concerning the stability of talc is lacking. Other physico-chemical variables, which are almost impossible to control experimentally, and difficult to

evaluate, are the fluctuations of pressure and gas composition that probably occur in the course of contact metamorphism. Included in these variables are solution equilibria, distribution of species in solution, and chemical potentials of mobile components. These factors essentially govern metasomatic processes, and since fluorine and boron are regarded as elements which enter readily into volatile compounds, conditions of mobilization must be significant to the formation of humite minerals and fluoborite. The general mobility of fluorine has been paid attention to by many petrologists (cf. Harker 1932), but precise treatment of its behaviour during metamorphism has not been established. According to Miyashiro (1967) the type of metasomatism might be expected to be closely related to the metamorphic facies under which it takes place. Although metasomatism should have some connection with the stability relations of minerals as represented by metamorphic facies, the behaviour of introduced elements also depends on what kind of material they are introduced into. Hydrothermal processes involving introduction of fluorine into silicate rocks may cause diffuse zones of fluorine dispersion (e.g. Hübner 1968). If, on the other hand, fluorine is introduced into a dolomite, humite mineral formation may restrict its mobility. Field studies of humite mineral parageneses in siliceous dolomites indicate that fluorine bearing phases are restricted to relatively narrow areas in the inner parts of the contact aureole. In the contact aureole of Suian, Korea (Watanabe op.cit.) the humite minerals mainly occur with forsterite and are restricted to a zone between 50 and 200 m from the contact. Silicate reactions resulting in development of

diopside, tremolite, and forsterite have occurred in a zone that extends up to 1 km from the contact. The contact skarns described by Tilley (1951 a) show a more complex appearance, but the mineral assemblages indicate that the mobility of fluorine is strongly restricted in dolomite.

The experiments show that a significant increase in the proportion of silica in the system effectively hinders the development of chondrodite at temperatures too low to allow formation of tremolite, diopside, and forsterite. Accordingly the results do not provide evidence of any catalytic efficacy of fluorine in causing appearance of forsterite, diopside, or tremolite at temperatures lower than those normally required for their crystallization. Contrary to such presumptions the experimental data suggest that silica dissolved in the gas phase affects the formation of humite minerals. The distribution of mineral phases in the marble of Frasco (Trommsdorff op.cit.) conforms well with this interpretation of the experimental results. The paragenesis in the marble is characterized by assemblages of skarn silicates appearing in narrow zones in a dolomite. The following outward sequence has been observed:

1. tremolite-diopside-calcite,
2. tremolite-calcite,
3. chondrodite-clinohumite-clinochlore-calcite-dolomite,
4. clinochlore-forsterite-calcite-dolomite.

The boundary between zone 2 and zone 3 is sharp. According to the interpretation of this skarn paragenesis metasomatic introduction of silica has occurred along joints in the dolomite. Assuming that this metasomatism included a

simultaneous outward flow of fluorine, the appearance of the fluorine-bearing phases conforms with the aspect that fluorine reactions strongly depend on the silica content of the metasomatic fluid. Close to the joints, where the gas phase was saturated with silica, tremolite and diopside developed. The reduction of the silica content of the gas phase caused by this skarn crystallization gave opportunity to humite mineral formation in zone 3.

The experimental data do not form any adequate basis of an analysis of the relations between fluoborite and humite minerals. For very low proportions of CO_2 in the gas phase fluoborite appears around 400°C. Already a moderate increase in the proportion of CO_2 causes a considerably weaker formation of fluoborite. Assuming that low values of P_{CO_2} have been maintained during boron-fluorine metasomatism, the data regarding stability of humite minerals suggest that the metasomatic fluids were undersaturated with respect to silica. Alternatively the formation of humite minerals and fluoborite was not physico-chemically connected.

It has been claimed by various authors that fluorine plays a significant role as carrier of metals in hydrothermal ore deposition (cf. Goldschmidt 1954, and Geijer 1958). No attempts have been made in this study to deal with such aspects. It is, however, apparent that the stability of fluorine- and boron-bearing phases is affected by the composition of the metasomatic solutions. Although a dolomitic body to a certain extent acts like a blotting paper on magmatic fluids, there is a considerable scope of variation in the appearance of mineral phases within this blotting paper. The available evidence indicates that humite mineral parageneses

may be useful in interpretations of contact metamorphic processes involving metasomatism.

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Table 1. Powder diffraction patterns for chondrodite.

This investigation[1] CuK$_\alpha$		van Valkenburg NBS Cu 1.5405 Å		Sahama, Hangelby Cu 1.5405 Å		Kowalski Zlotego Stoku	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
----	---	7.418	10	----	---	----	---
----	---	-----	---	----	---	4.93	5
4.87	26	4.854	40	4.83	s	----	---
4.00	11	3.992	20	----	---	4.038	2
----	---	3.948	18	----	---	-----	---
----	---	3.897	11	3.92	w	-----	---
----	---	3.685	23	3.69	w	-----	---
3.58	35	3.554	42	3.55	m	3.567	2
3.49	32	3.477	30	3.47	m	-----	---
3.39	24	3.390	27	3.37	m	3.419	1
----	---	-----	---	----	---	3.263	1
----	---	-----	---	----	---	3.145	1
3.00[2]		3.007	45	3.00	s	3.019	10
----	---	2.910	15	2.91	vw	-----	---
2.85	24	2.842	15	2.83	w	-----	---
2.76	52	2.764	35	2.75	m	2.776	3

Table 1 continued.

d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
----	---	-----	---	----	---	2.725	1
2.68	36	2.672	43	2.66	s	2.644	3
2.62	57	2.605	57	2.61	m	2.627	3
2.53	55	2.512	41	2.50	s	2.533	4
----	---	2.461	11	----	---	-----	---
2.43	14	2.428	18	2.42	w	2.420	2
2.33	23	2.318	27	2.31	m	-----	---
2.29[2)]		2.301	21	2.29	w	2.300	10
----	---	2.272	100	2.27	m	-----	---
2.26	100	2.252	100	2.25	vs	-----	---
----	---	-----	---	----	---	2.184	1
2.15	7	2.149	16	2.14	vw	-----	---
2.12	15	-----	---	2.10	vw	-----	---
----	---	2.025	9	----	---	2.037	2
----	---	2.009	10	----	---	-----	---
----	---	1.945	9	----	---	-----	---
----	---	1.882	8	----	---	-----	---
----	---	1.851	9	----	---	-----	---

Table 1 continued.

d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
----	---	1.795	16	1.790	vw	1.808	1
----	---	1.789	16	-----	---	-----	---
1.744	94	1.737	98	1.735	s	1.751	4
-----	---	1.693	16	1.688	vw	1.701	1
-----	---	1.633	5	-----	---	-----	---
1.62	2	1.617	18	1.611	w	1.626	2
1.60	3	1.603	11	-----	---	-----	---
----	---	1.574	12	1.570	vw	-----	---
----	---	1.561	5	-----	---	1.553	1
----	---	1.542	6	-----	---	-----	---
----	---	-----	---	1.498	vw	1.511	1
----	---	-----	---	1.478	m	1.467	1
----	---	-----	---	1.395	vw	1.400	1
----	---	-----	---	1.340	m	-----	---

1) 2 ~~θ~~-values are converted to d-values after Fang and Bloss (1966).

2) Reflexions overlapped by calcite reflexions.

Table 2. Run data at 10500 P.S.I. (700 Bars).
Open system ($X_{CO_2} = 0, P_f = P_{H_2O}$).
Starting material: 3 dolomite + 1 quartz + 1 fluorite.

Run	Time (Days)	Temp (°C)	Crystalline products
14	32	672	Ch,Cc,(F)
17	32	353	Ch,Cc,(Dol)(F)
18	28	485	Ch,Cc,(F)
29	25	292	Dol,Cc,Tc,(F)
51	33	465	Ch,Cc,Tc,(F)
54	60	322	Dol,Cc,F,Bc,S,(Ch)
43[1)]	23	465	Ch,Cc,(Dol)(F)

1) Starting material: 9 dolomite + 1 quartz + 3 fluorite.

Table 3. Run data at 15000 P.S.I. (1035 Bars).
Open system ($X_{CO_2} = 0, P_f = P_{H_2O}$).
Starting material: 3 dolomite + 1 quartz + 1 fluorite.

Run	Time (Days)	Temp (°C)	Crystalline products
23	22	550	Ch,Cc,(F)
39	15	430	Ch,Cc,(F)
49	24	390	Ch,Cc,(Dol)(F)
53	34	401	Ch,Cc,(F)
63	30	375	Ch,Cc,Dol,(F)
70	57	355	Ch,Cc,(F)
80	54	342	Dol,Cc,F,(Ch)

Table 4. Run data at 22500 P.S.I. (1550 Bars).

Open system ($X_{CO_2} = 0, P_f = P_{H_2O}$).

Starting material: 3 dolomite + 1 quartz + 1 fluorite.

Run	Time (Days)	Temp (°C)	Crystalline products
35[1)]	21	490	Ch,Dol,Cc,(F)
36	21	490	Ch,Cc,(F)
64	31	482	Ch,Cc
72	35	443	Ch,Cc,(F)
76	80	410	Ch,Cc,(F)
77	80	400	Ch,Dol,Cc,F,Tc
81	60	392	Ch,Cc,F,Tc,(Dol)
82	60	365	Cc,Dol,F,Tc

1) Starting material: 9 dolomite + 1 quartz + 1 fluorite.

Table 5. Run data at 30000 P.S.I. (2070 Bars).

Starting material: 3 dolomite + 1 quartz + 1 fluorite.

Run	Time (Days)	Temp (°C)	Crystalline products	Mole fraction X_{CO_2}
60	21	500	Ch,Cc,Tc,(F)	0.00
66	65	505	Dol,Cc,(Ch)(Tc)(F)	0.94
67	65	490	Dol,Cc,Tc,F	0.47
68	65	450	Ch,Cc	0.00
75	74	447	Ch,Cc,(F)	0.00
78	72	532	Ch,Cc,(Dol)(F)	0.95
79	72	490	Dol,Cc,Tc,F	0.59
83	60	395	Ch,Cc,(Dol)(F)	0.00
85	53	480	Dol,Cc,Tc,F	0.26
86	60	495	Dol,Cc,Tc,F	0.41
88	60	372	Dol,Cc,(Ch)(F)	0.00
89	60	385	Ch,Cc,(Dol)(F)	0.00
90	60	468	Dol,Cc,F,(Ch)(Tc)	0.29
91	60	445	Dol,Cc,Tc,F	0.07

Table 6. Run data at 30000 P.S.I. (2070 Bars).
Starting material: 5 dolomite + 2 quartz + 1 fluorite.

Run	Time (Days)	Temp (^{o}C)	Crystalline products	Mole fraction X_{CO_2}
92	58	512	Ch,Cc,Tc,(F)	0.68
93	58	500	Ch,Cc,Tc,(Dol)(F)	0.36
94	43	530	Ch,Cc,F	0.51
96	34	513	Ch,Cc,Dol,Tc,(F)	0.85
98	60	490	Ch,Cc,Tc,(Dol)(F)	0.24
101	50	477	Dol,Cc,Tc,F,(Ch)	0.26
102	30	446	Dol,Tc,F,(Cc)	0.17
103	30	453	Dol,Cc,Tc,F	0.18
114	46	505	Dol,F,(Ch)(Cc)	0.99

Table 7. Run data at 30000 P.S.I. (2070 Bars).
Starting material: 1 talc + 7 dolomite + 2 fluorite.

Run	Time (Days)	Temp (^{o}C)	Crystalline products	Mole fraction X_{CO_2}
95	28	455	Ch,Cc,Tc,F,(Dol)	0.08
100	2	465	Ch,Cc,Tc,F	0.04
106	50	518	Ch,Cc,(Tc)(F)	0.24
107	50	500	Dol,Cc,Tc,(Ch)	0.66
108	45	475	Cc,Tc,(Dol)(F)	0.17
109	45	465	Ch,Cc,Tc,(Dol)(F)	0.12
112	26	440	Ch,Cc,Dol,Tc,F	0.05
113	46	490	Dol,Tc,F,(Cc)	0.99
115	10	415	Dol,Tc,F,(Cc)	0.04
116	10	390	Dol,Tc,F,(Cc)	0.02
117	33	455	Ch,Cc,Tc,(Dol)	0.08
118	33	474	Ch,Cc,Tc	0.10
121	40	480	Ch,Cc,Tc	0.18

Table 8. Run data at 30000 P.S.I. (2070 Bars). Reversed reactions.

Starting material: 5 dolomite + 2 quartz + 1 fluorite (run 104 and 105)

1 talc + 7 dolomite + 2 fluorite (run 110, 111, 119, and 120).

Run	Fluorine reaction Time (Days)	Fluorine reaction Temp (°C)	Reversed reaction Time (Days)	Reversed reaction Temp (°C)	Crystalline products	Mole fraction X_{CO_2}
104	5	540	30	475	Cc,Tc,(Dol)(F)	0.51
105	5	540	30	453	Cc,(Dol)(F)	0.15
110	12	579	40	501	Ch,Cc,(Dol)(F)	0.99
111	14	560	40	472	Cc,Tc,(Dol)(F)	0.22
119	7	537	20	485	Ch,Cc	0.13
120	7	500	20	458	Cc,Tc,(Ch)	0.09

Table 9. Run data at 30000 P.S.I. (2070 Bars).

Starting material: 10 dolomite + 10 quartz + 1 fluorite.

Run	Time (Days)	Temp (°C)	Crystalline products	Mole fraction X_{CO_2}
131	12	520	Dol,Cc,Tc,F	0.65
132	12	540	Dol,Cc,Tc,F	0.41
133	27	540	Dol,Cc,Tc,F	0.60
134	27	480	Dol,Cc,Tc,F	0.65
135	13	560	Cc,Tc,F,(Ch)(Dol)	0.45
136	13	575	Ch,Cc,(Tr)	0.65
137	20	546	Ch,Cc,Tc,F,(Dol)	0.95
138	20	530	Cc,Tc,(Ch)(Dol)(F)	0.29
139	8	590	Ch,Cc,Di,(Tr)(Dol)(F)	0.51
140	8	575	Ch,Cc,Tr,(Di)(F)	0.43
141	64	537	Cc,Tc,F,(Ch)(Dol)	0.93
142	64	520	Cc,Tc,F,(Ch)(Dol)	0.15
143	45	555	Cc,Tc,F,(Ch)(Dol)	0.97
144	45	543	Ch,Tr,(Cc)(Di)	0.00
145	16	570	Ch,Tr,(Cc)	0.27
146	16	558	Cc,Tc,(Ch)(Tr)(F)	0.23
147	16	565	Cc,Tc,Dol,F,(Ch)	0.91
148	16	565	Cc,Tc,(Ch)(Dol)(F)	0.74
149	16	550	Ch,Cc,Tc,(F)	0.17
150	16	550	Ch,Cc,Tc,(F)	0.10
151	18	553	Cc,Tc,F,(Ch)(Dol)	0.33
152	17	584	Ch,Cc,Tc,F,(Dol)	0.66
153	21	558	Ch,Cc,Tr,Di,(F)(Dol)	0.22
154	21	545	Ch,Cc,Tc,(Dol)(F)	0.14
155	32	564	Ch,Cc,Tr,(Di)	0.14
156	56	520	Dol,Cc,Tc,F	0.28
157	56	520	Dol,Cc,Tc,F	0.53

Table 10. Run data at 30000 P.S.I. (2070 Bars).

Starting material: 1 tremolite + 13 dolomite + + 2 fluorite.

Run	Time (Days)	Temp (^{o}C)	Crystalline products	Mole fraction X_{CO_2}
161	30	560	Ch,Cc,Dol,Tr,(F)	0.74
162	30	560	Ch,Cc,(Tr)(F)	0.47
163	30	545	Ch,Cc,(Tr)(F)	0.00
164	15	557	Ch,Cc,(Dol)(Tr)(F)	0.22
165	22	583	Ch,Cc,(Tr)(F)	0.00
166	15	510	Dol,Tr,(Ch)(Cc)(F)	0.15
167	15	523	Dol,Tr,(Ch)(Cc)(F)	0.55
168	27	536	Dol,Tr,(Ch)(Cc)(F)	0.90
169	27	536	Ch,Cc,Dol,(Tr)(F)	0.44
170	34	505	Ch,Cc,Dol,(Tr)(F)	0.27
171	34	495	Dol,Tr,(Ch)(Cc)(F)	0.13
172	35	525	Dol,Tr,(Ch)(Cc)(F)	0.79
173	35	525	Dol,Tr,(Ch)(Cc)(F)	0.90
174	35	515	Ch,Cc,(Dol)(Tr)(F)	0.00
175	22	523	Ch,Cc,(Dol)(Tr)(F)	0.35
176	30	510	Dol,Tr,(Ch)(Cc)(F)	0.43
177	36	510	Ch,Cc,(Dol)(Tr)(F)	0.20
178	30	500	Dol,Tr,F	0.47
179	30	485	Dol,Tr,F	0.36

Table 11. Thermodynamic data for calculation of the equilibrium constant, Kp, as a function of temperature at P_f = 2000 Bars.

Temp (°C)	$\frac{10^3}{T}$ °K^{-1}	Mole fraction obtained from figure 2. X_{CO_2}	X_{H_2O}	$f^*_{CO_2}$(Bars)	$f^*_{H_2O}$(Bars)	$\log Kp = 5 \log f_{CO_2} + \log f_{H_2O}$
400	1.486	0.01	0.99	3540	406	10.35
410	1.464	0.015	0.985	3586	433	11.28
420	1.443	0.025	0.975	3614	448	12.42
430	1.422	0.035	0.965	3636	484	13.19
440	1.403	0.05	0.95	3656	512	14.00
450	1.383	0.075	0.925	3670	542	14.90
460	1.364	0.105	0.895	3684	567	15.64
470	1.346	0.15	0.85	3694	606	16.43
480	1.328	0.21	0.79	3702	640	17.16
490	1.311	0.30	0.70	3710	673	17.91
500	1.294	0.45	0.55	3716	712	18.72

$f^*_{CO_2}$ and $f^*_{H_2O}$: fugacities of the pure gases CO_2 and H_2O respectively.

Table 12. Run data at 30000 P.S.I. (2070 Bars).

Starting material: 6 dolomite + 1 fluorite + B_2O_3.

Run Fb series	Time (Days)	Temp (°C)	Crystalline products	Mole fraction X_{CO_2}
1	11	600	Fb,Cc,(F)	0.24
2	25	540	Fb,Cc,(F)	0.23
3	30	500	Fb,Cc,(F)(Dol)(B_2O_3)	0.20
4	20	512	Fb,Cc,(F)	0.00
5	40	530	Fb,Cc,(F)(Dol)(B_2O_3)	0.85
6	45	500	Fb,Cc,(F)(Dol)(B_2O_3)	0.22
7	20	461	Fb,Cc,(F)	0.00
8	20	413	Fb,Cc	0.00
9	25	351	Dol,F,B_2O_3	0.00
10	23	515	Fb,Cc,(F)(Dol)	0.25
11	44	493	Fb,Cc,(F)(Dol)(B_2O_3)	0.25
12	38	474	Fb,Cc,(F)(Dol)(B_2O_3)	0.28
13	31	378	Dol,F,B_2O_3	0.00
14	21	500	Fb,Cc,(F)(Dol)(B_2O_3)	0.37
15	40	467	Dol,F,(Fb)(Cc)(B_2O_3)	0.72
16	30	440	Fb,Cc,(F)(Dol)(B_2O_3)	0.09
17	30	395	Fb,Cc,(F)(Dol)(B_2O_3)	0.00
18	53	485	Fb,Dol,(F)(Cc)(B_2O_3)	0.85
19	53	496	Dol,(F)(Fb)(Cc)(B_2O_3)	0.56
20	65	425	Dol,F,B_2O_3,(Fb)(Cc)	0.16
21	65	435	Dol,F,B_2O_3,(Fb)(Cc)	0.31
22	22	420	Dol,F,B_2O_3	0.68
23	22	410	Dol,F,B_2O_3	0.28
24	21	545	Dol,F,B_2O_3,(Fb)(Cc)	0.53
25	21	558	Dol,F,(Fb)(Cc)(B_2O_3)	0.45
26	32	580	Fb,Cc,(F)	0.32
27	30	540	Fb,Cc,(F)	0.14
28[1]	35	445	Dol,F,B_2O_3	0.27
29[1]	35	450	Dol,F,B_2O_3	0.43
30[1]	28	470	Dol,F,B_2O_3,(Fb)(Cc)	0.37
31[1]	35	429	Dol,F,B_2O_3	0.21
32[1]	30	449	Dol,F,B_2O_3,(Fb)(Cc)	0.17

1) Initially added benzoic acid.

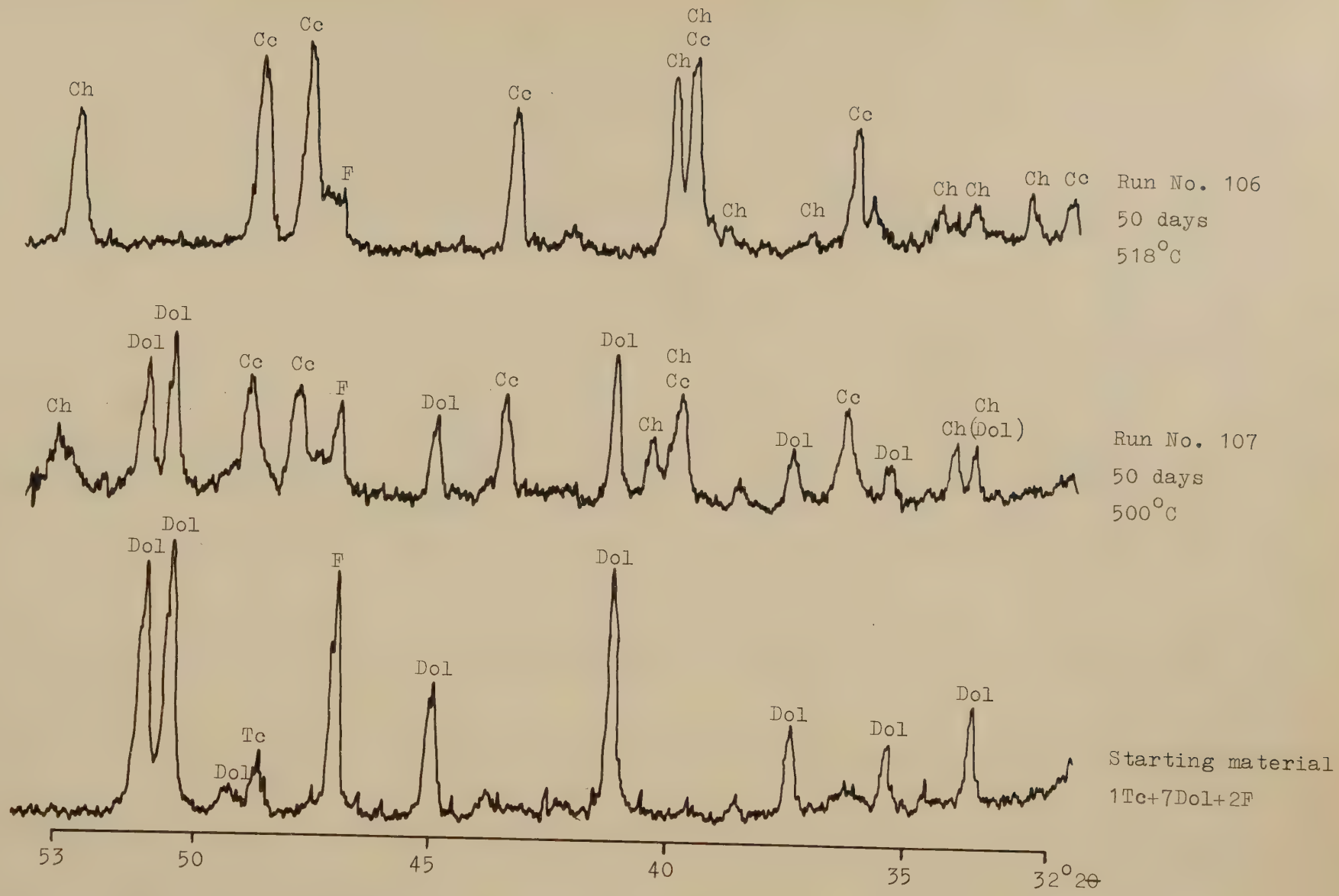


Fig. 1. X-ray diffraction patterns of starting materials 1Tc+7Dol+2F, reaction products representing incomplete fluorine reaction (run No. 107), and reaction products representing complete conversion to chondrodite and calcite (run No. 106).

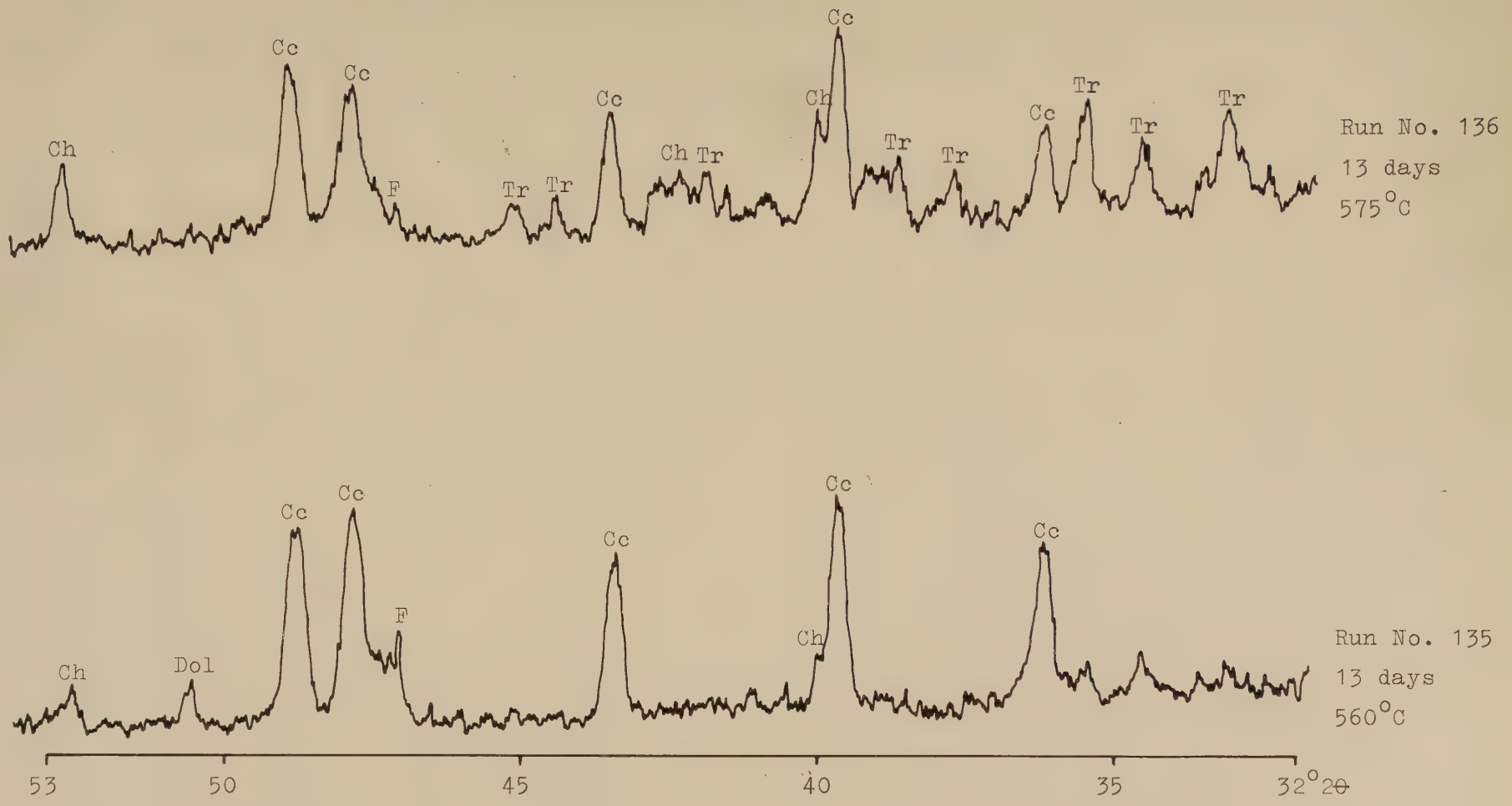
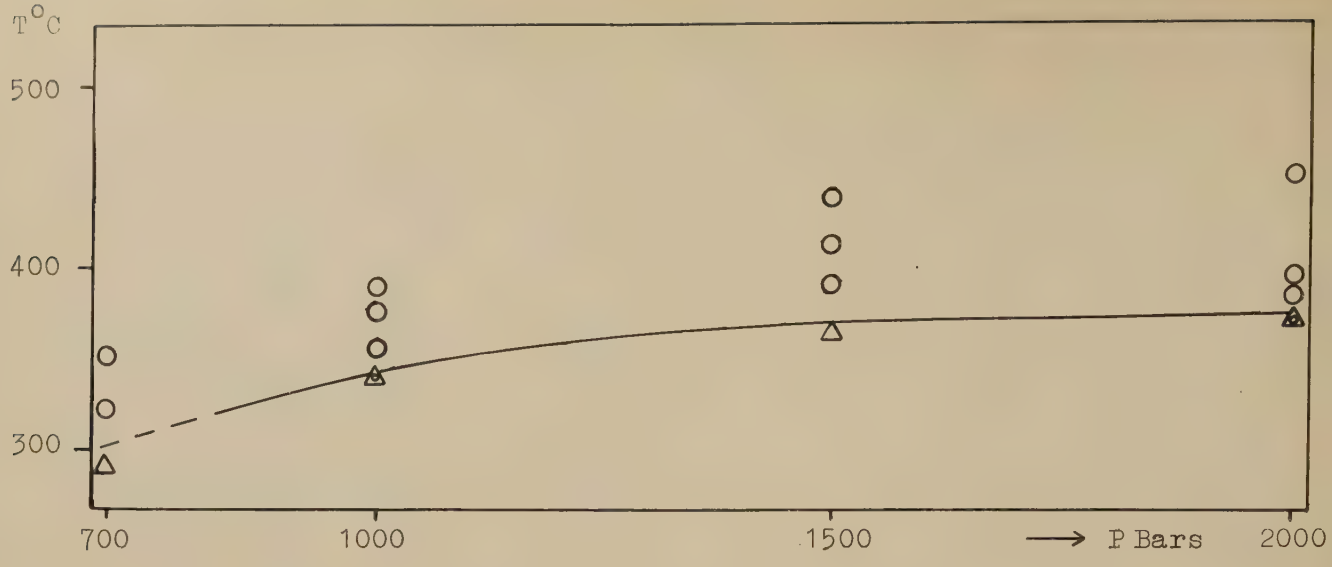
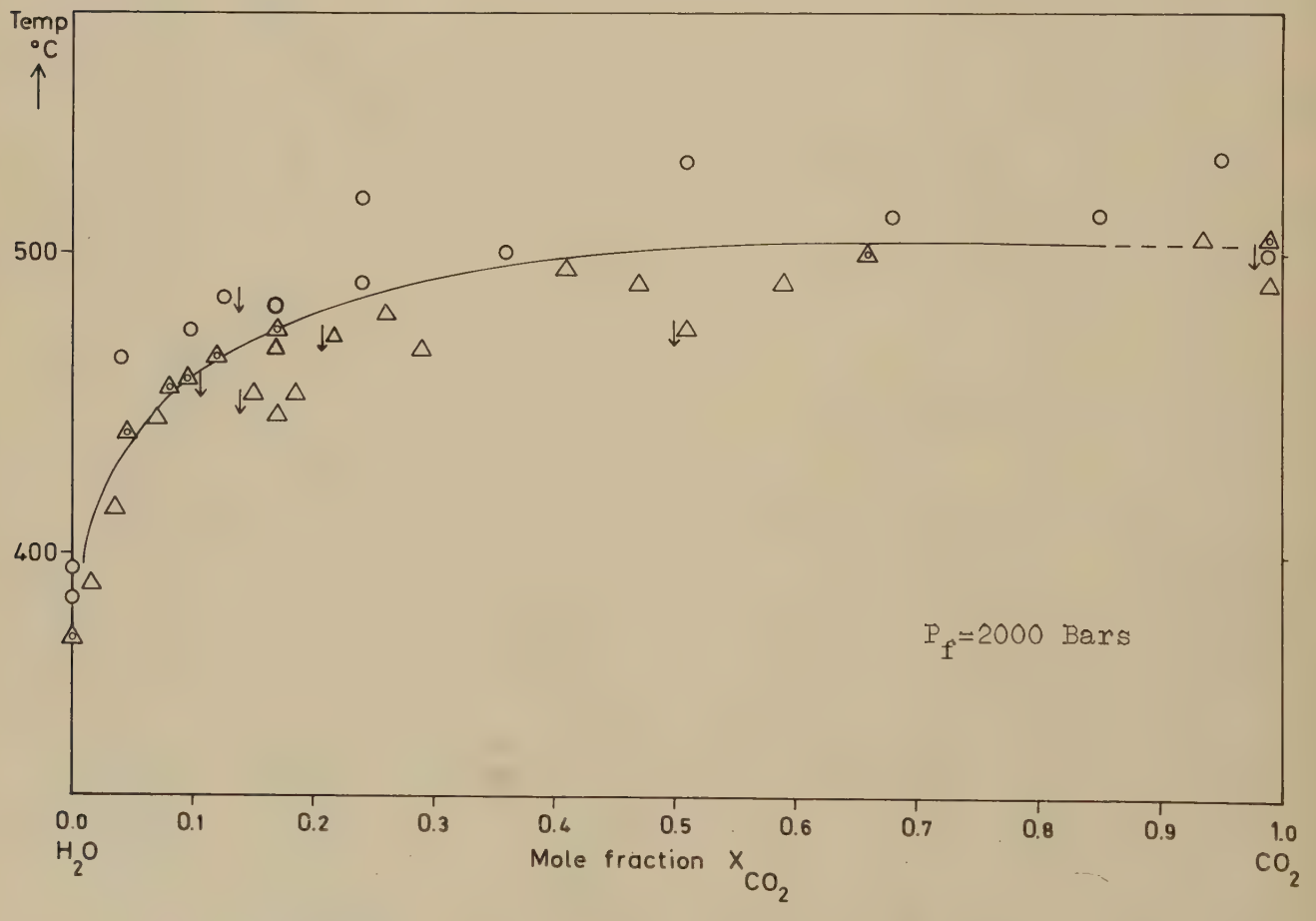


Fig. 2. X-ray diffraction patterns showing the influence of excess silica on chondrodite formation. Despite higher reaction temperatures fluorination reactions in a system consisting of dolomite, quartz, and fluorite in the proportions 10/10/1 are weaker than corresponding reactions in more silica-deficient systems.



Symbols: △ Tc,Dol,F ▲ Tc,Dol,F,(Cc)(Ch) ○ Ch,Cc

Fig. 3. Temperature-composition diagram showing the phase boundary for chondrodite for the case in which $P_f = P_{H_2O}$.



Symbols: △ Tc,Dol,F ▲ Tc,Dol,F,(Cc)(Ch) ○ Ch,Cc

Fig. 4. Isobaric temperature-composition diagram showing the phase relations between starting materials and chondrodite for the case in which $P_f = P_{H_2O} + P_{CO_2}$.

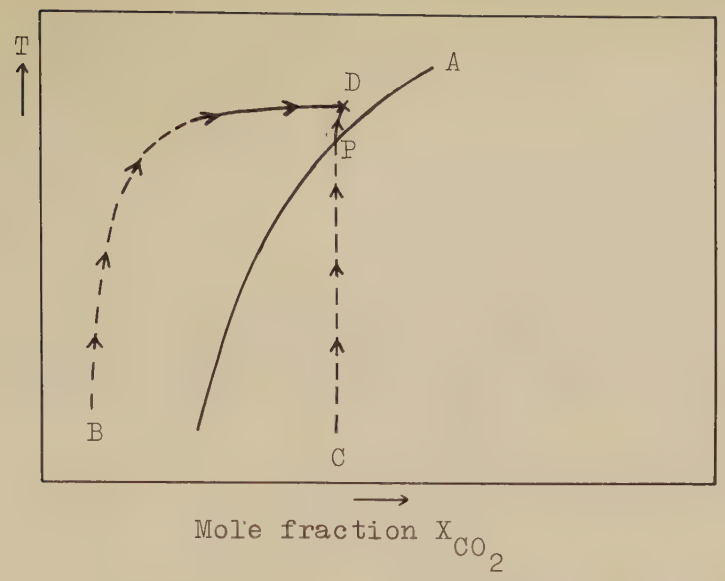
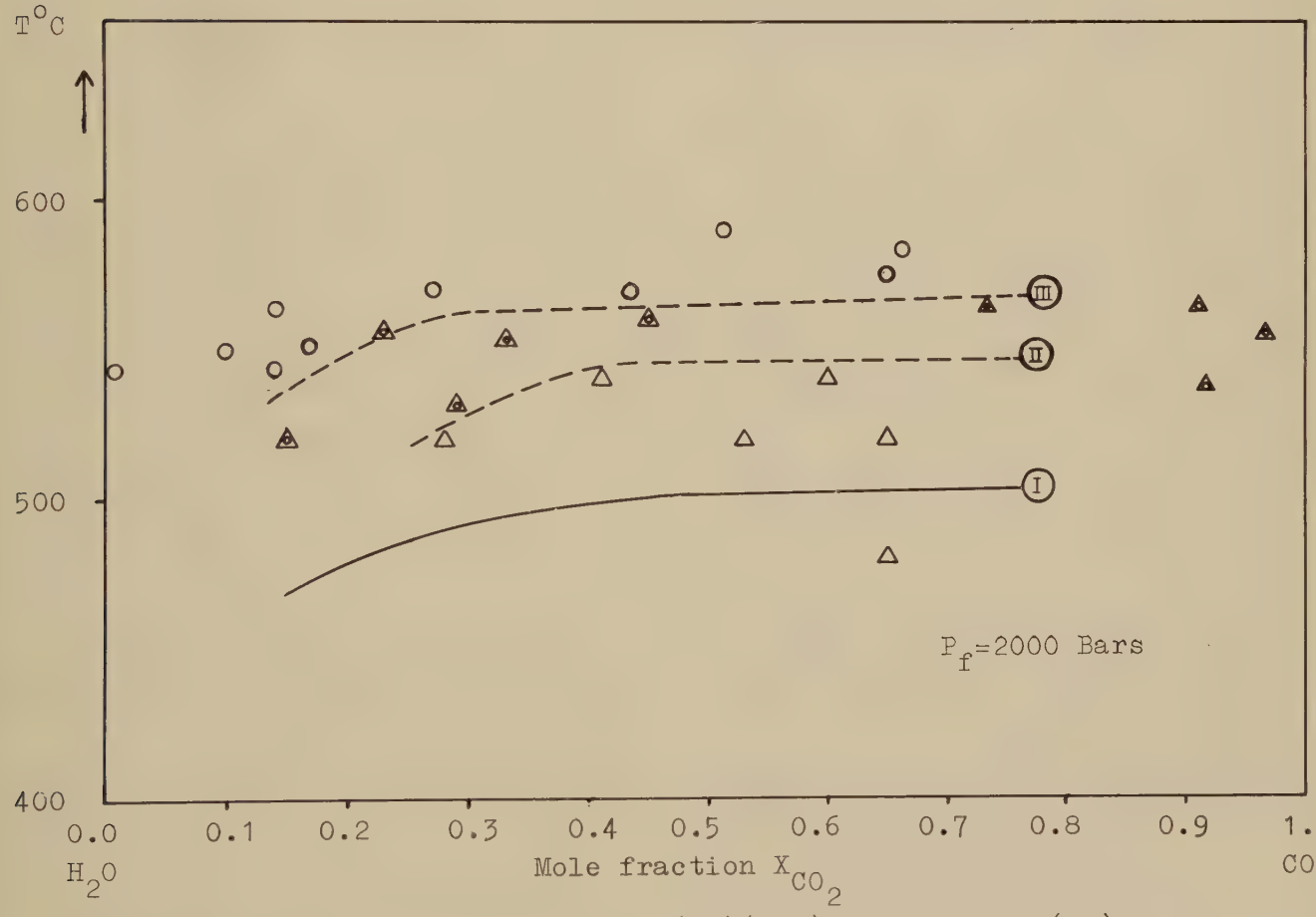


Fig. 5. Diagram showing two possible paths of reaction in runs characterized by low values of P_{H_2O}. The curve A represents the stability boundary of chondrodite. Reaction along BD results in a more distinct appearance of chondrodite than a corresponding physico-chemical development along CPD.



Symbols: △ Tc,Cc,F,Dol ▲ Tc,Cc,F,(Ch)(Dol) ○ Ch,Cc,Tr,(Di)

Fig. 6. Isobaric temperature-composition diagram showing the phase boundary of chondrodite in a system with excess silica. Curve I is the phase boundary of fig. 4. The field between curve II and curve III represents weak chondrodite formation. Above curve III chondrodite coexists with tremolite.

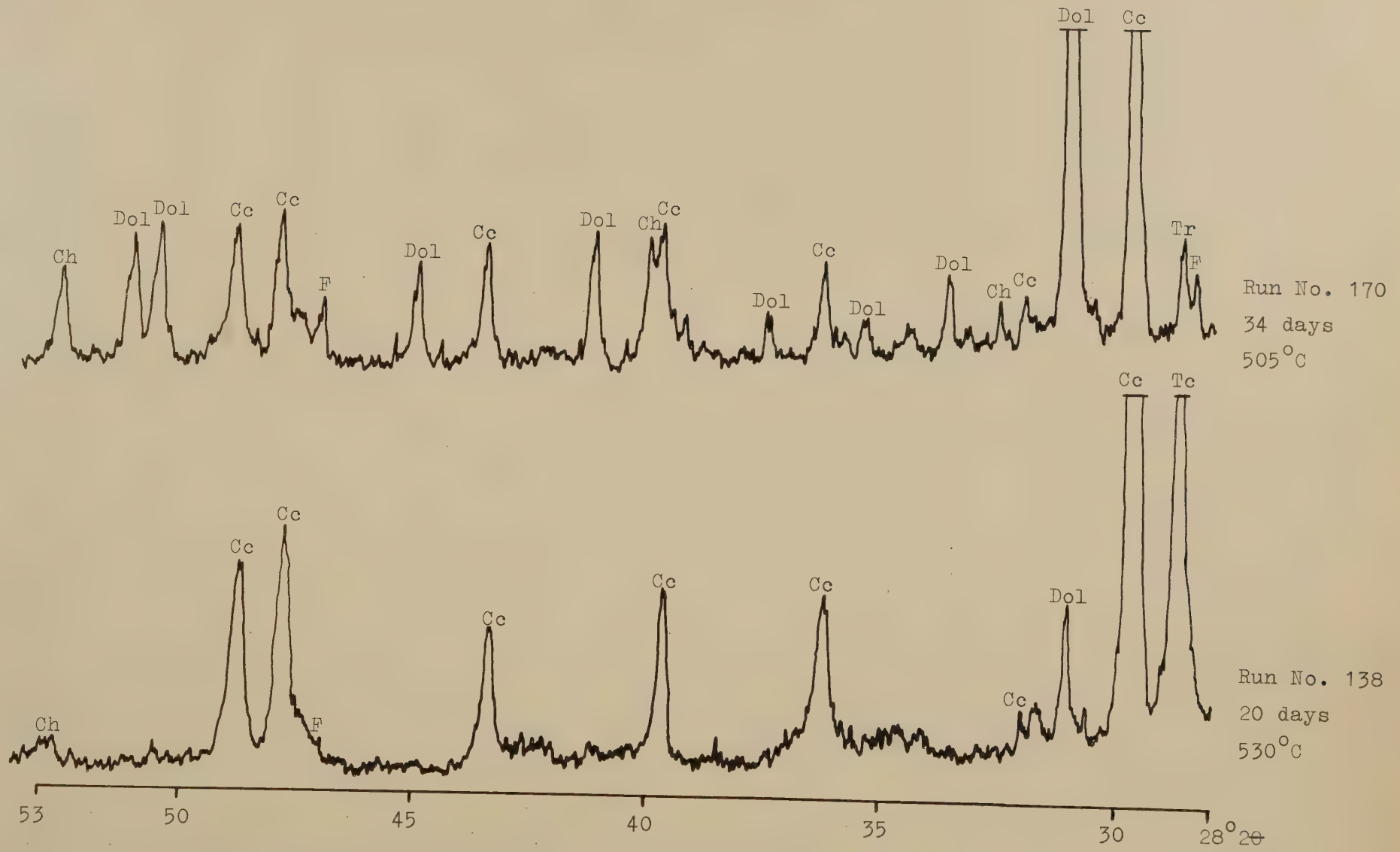


Fig. 7. X-ray diffraction patterns of reaction products of run number 138 (starting materials: 10Dol+10Q+1F), and run number 170 (starting materials: 1Tr+13Dol+2F).

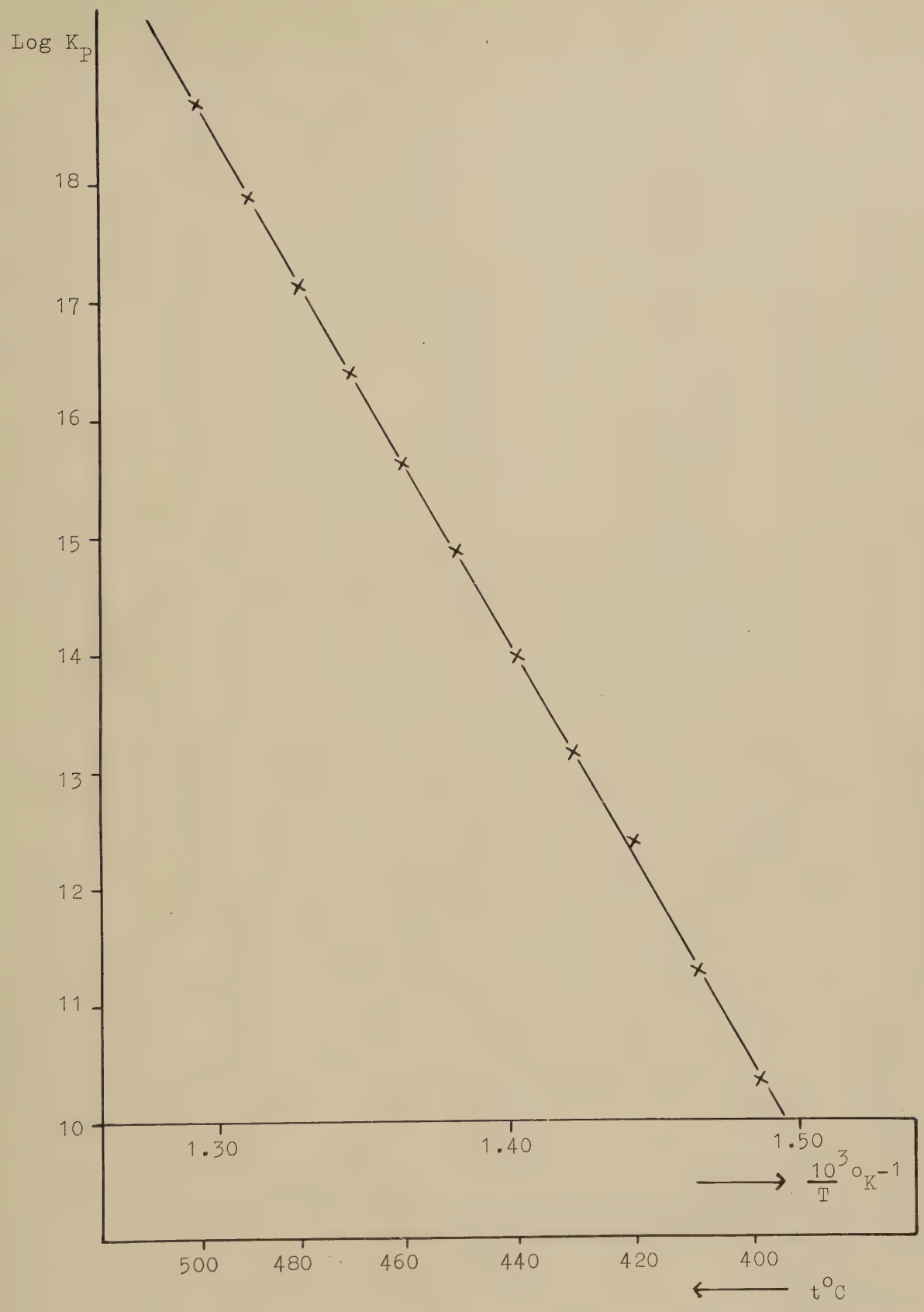
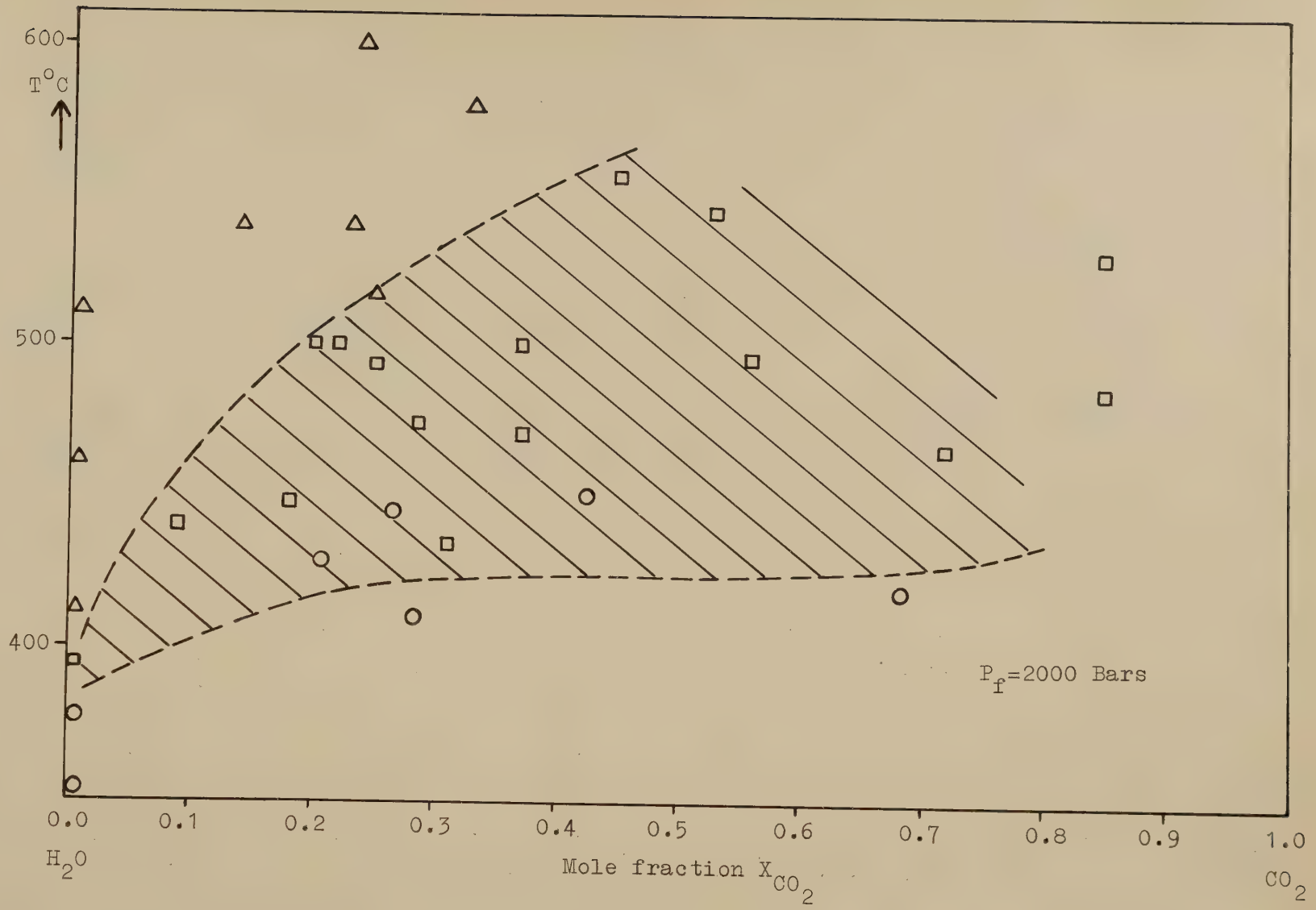


Fig. 8. log K_P=5 log P_{CO_2} +log P_{H_2O} plotted as a function of inverse temperature.



Symbols: ○ Dol,F,B_2O_3 □ Dol,F,B_2O_3,(Fb)(Cc) △ Fb,Cc

Fig. 9. Isobaric temperature-composition diagram showing the incomplete character of fluoborite formation. The striated area represents weak fluoborite formation.

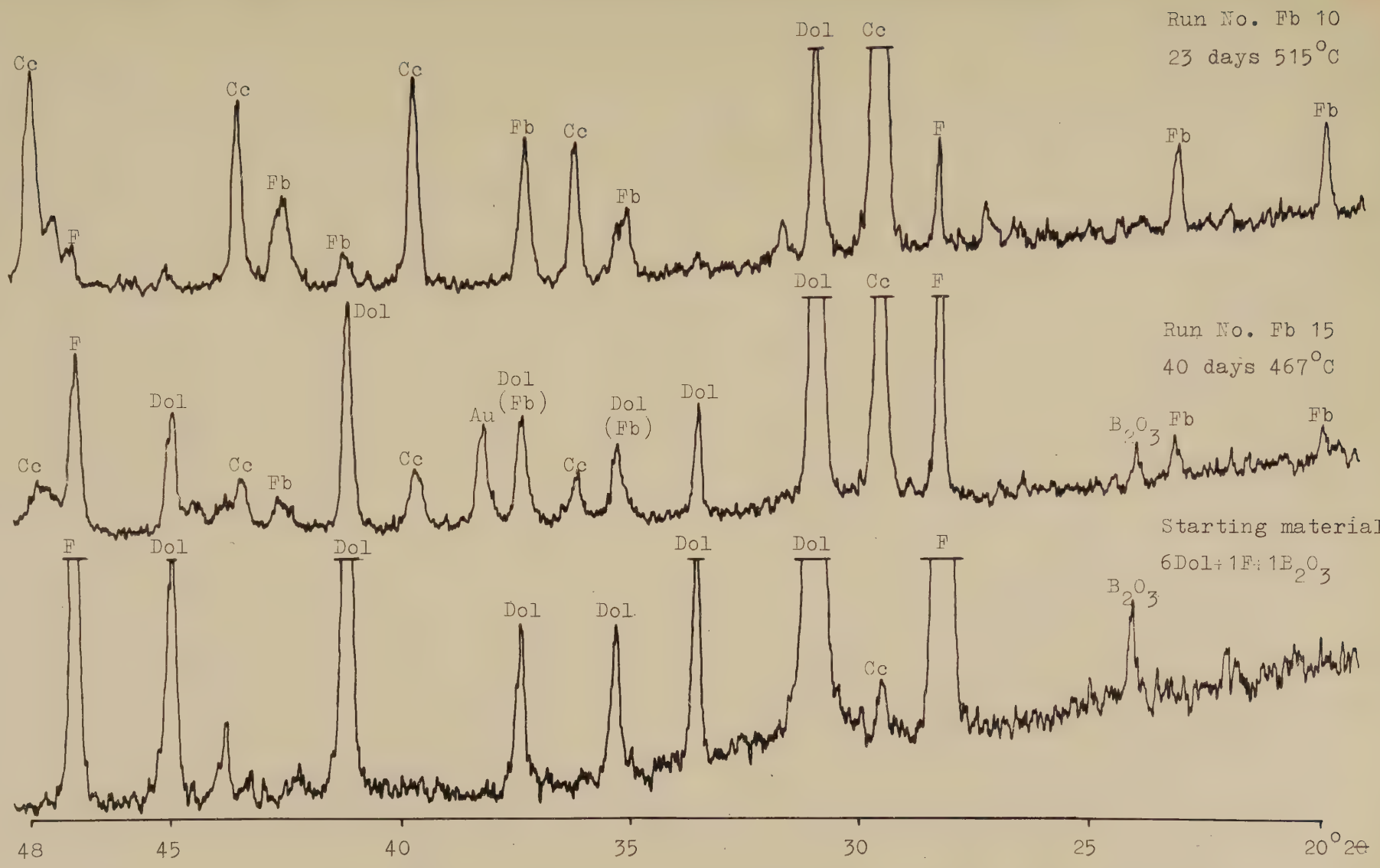


Fig. 10. X-ray diffraction patterns of the starting materials 6Dol+1F+1B_2O_3, reaction products representing incomplete boron reaction (run No. Fb 15), and reaction products representing almost complete conversion to fluoborite (run No. Fb 10).

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